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Thesis

THE PREPARATION AND PROPERTIES OF SOME POLYURETHANES

By

Walter Olds
(B.S., University of Connecticut 1944)
submitted in partial fulfilment of the
requirements for the degree of
Master of Arts

1947

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Approved

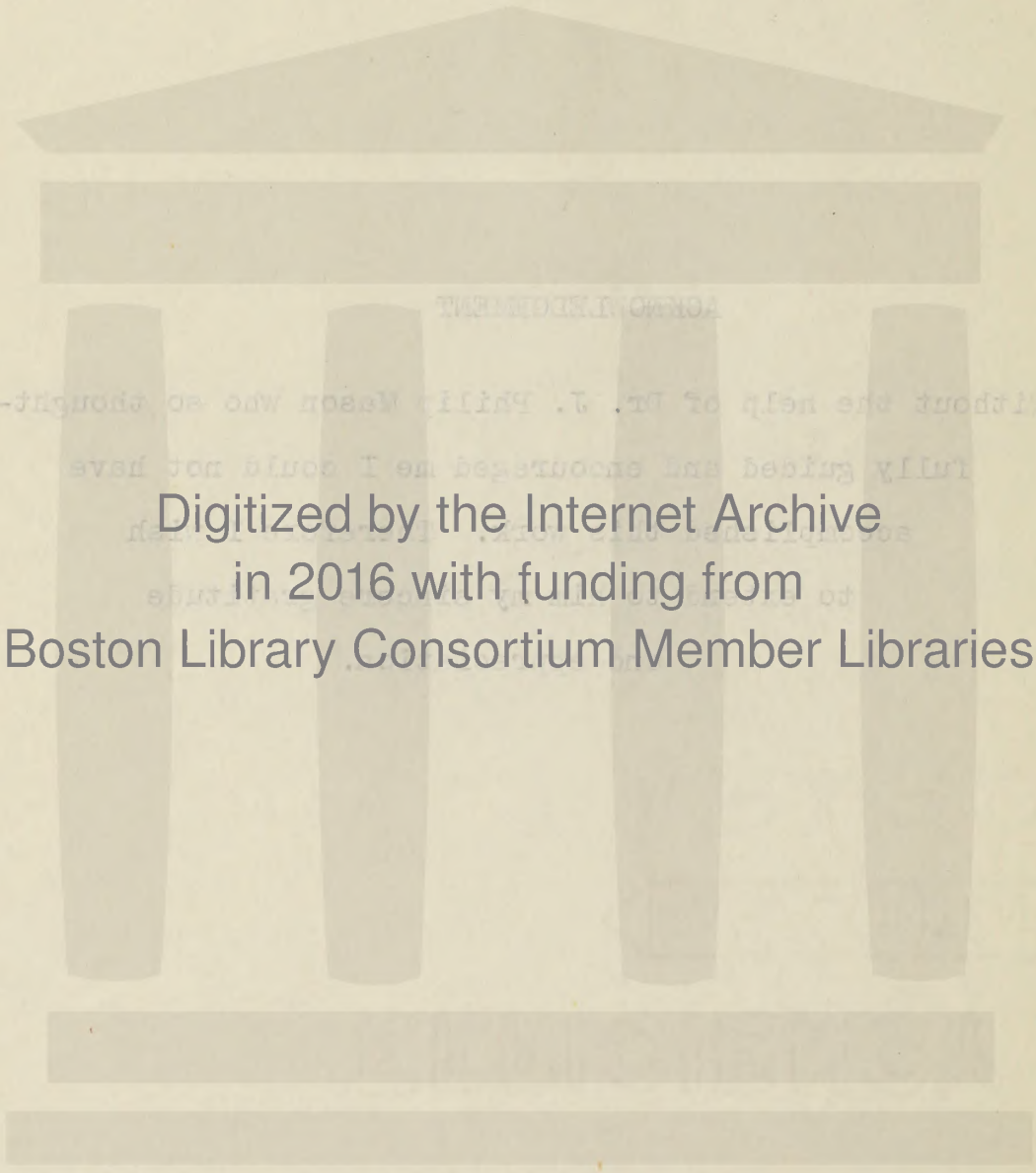
by

First Reader J. Philip Mason
Professor of Chemistry

Second Reader Richard H. Bailes
Professor of Chemistry

ACKNOWLEDGEMENT

Without the help of Dr. J. Philip Mason who so thoughtfully guided and encouraged me I could not have accomplished this work. Therefore I wish to extend to him my sincere gratitude and appreciation.



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TOPICAL OUTLINE

Page

Introduction..... 1

Previous Methods of Preparation.....

Problem .....

Experimental.....

Polymer I..... 4

Preparation..... 4

Properties.....7

Hydrolysis Products.....8

Purification.....10

Molecular Weights

Fractionated Once.....16

Fractionated Three Times.....17

Polymer II

Preparation.....18

Molecular Weights

Original Product.....19

After adding additional chloroformate.....20

Polymer III.....22

Polymer IV.

Preparation.....24

Molecular Weights

Fractionated Once.....28

Fractionated Three Times.....29

Polymer V

Preparation.....31

TOPICAL OUTLINE

Page

Introduction..... 1

Previous Methods of Preparation.....

Problem .....

Experimental.....

Polymer I..... 4

Preparation..... 4

Properties.....7

Hydrolysis Products.....8

Purification.....10

Molecular Weights

Treatment Once.....16

Treatment Three Times.....17

Polymer II

Preparation.....18

Molecular Weights

Original Product.....19

After adding additional chloroformate.....20

Polymer III.....22

Polymer IV.

Preparation.....24

Molecular Weights

Treatment Once.....28

Treatment Three Times.....29

Polymer V

Preparation.....31

Experimental Page

Viscosity-Molecular Weight Relationship..... 34

Polymer VI

Preparation..... 37

Properties..... 37

Polymer VII

Preparation..... 38

Properties..... 39

Findings and Conclusions..... 40

Summary..... 43

Bibliography..... 45

Experimental ..... Page
Viscosity-Molecular Weight Relationship 34
Polymer VI
Preparation 37
Properties 37
Polymer VII
Preparation 38
Properties 39
Findings and Conclusions 40
Summary 43
Bibliography 45

INTRODUCTION

Polyurethanes have been prepared by the addition of diisocyanates to glycols or polyhydroxy compounds (1, 2);

$$HO\text{-}R\text{-}OH + O{=}C{=}H\text{-}R\text{-}N{=}C{=}O \longrightarrow -O\text{-}R\text{-}O\text{-}CO\text{-}NH\text{-}R\text{-}NH\text{-}CO-$$

and by the condensation of the sodium salts of unsaturated acid amides with polychloroformates of polyhydroxy compounds and the subsequent polymerization through the double bond by means of heat, light, peroxides, etc. (3)

$$CH_2{=}CH\text{-}CO\text{-}NH\text{-}Na + Cl\text{-}CO\text{-}O\text{-}C_2H_4\text{-}O\text{-}CO\text{-}Cl \longrightarrow$$

$$CH_2{=}CH\text{-}CO\text{-}NH\text{-}CO\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}CO\text{-}NH\text{-}CO\text{-}CH{=}CH_2 + NaCl$$

Linear polymers prepared by the former method proved to be very versatile plastics with some properties superior to those of the superpolyamides and are suitable for the production of fibers, plastics, and especially bristles (4,5). The monomers of the type,

$$CH_2{=}CH\text{-}CO\text{-}NH\text{-}CO\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}CO\text{-}NH\text{-}CO\text{-}CH{=}CH_2$$

(1) U. S. Patent 2 266 777 to Theodore Lieser, Germany

(2) U. S. Patent 2 284 637 Willard E. Catlin to E. I. DuPont de Nemours Co.

(3) U. S. Patent 2 401 549 Albert G. Chenicek to Pittsburgh Glass Co.

(4) "Polyurethanes in Germany 1939-1945" Modern Plastics, Volume 23, No. 2, 152F (1945)

(5) "Polyurethanes" by Dr. Otto Bayer of Farbenind, Modern Plastics, Vol. 24, No. 10, 149 (1947). Translation of report presented in Frankfurt on September 24, 1941 and again on Nov. 21, 1941 at the 25th Kuko (Plastics Committee) meeting.

(1) U. S. Patent 2 [illegible] to Theodore Glaser, Germany

(2) U. S. Patent 2 [illegible] Willard B. Castle to E. I. Du Pont de Nemours Co.

(3) U. S. Patent 3 [illegible] Albert G. Chemlock to Pittsburgh Glass Co.

(4) "Polyurethanes in Germany 1939-1945" Modern Plastics, Volume 23, No. 6, 109 (1946)

(5) "Polyurethanes" by Dr. Otto Bayer of Farbenind. Modern Plastics, Vol. 24, No. 10, 149 (1947). Translation of lecture presented in Frankfurt on September 28, 1941 and again on Nov. 21, 1941 at the 35th Kunststoffe (Plastics Committee) meeting.

may be cast polymerized by heating under pressure in a mold to form solids of any desirable shape or may be partially polymerized to a fusible powder and molded by injection or fusion under pressure.

This paper describes the preparation of some linear polyurethanes by the condensation of a diamine with diethylene glycol bis-chloroformate, some of the properties of the products, and a method of determining the molecular weights of the products.

$$NH_2\text{-}R\text{-}NH_2 + Cl\text{-}CO\text{-}O\text{-}C_2H_4\text{-}O\text{-}CO\text{-}Cl \longrightarrow$$

$$\text{-}NH\text{-}R\text{-}NH\text{-}CO\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}CO\text{-} + HCl$$

Either an aqueous solution of sodium hydroxide or an excess of the diamine was used to combine with the hydrogen chloride liberated.

It was believed that the condensation product of the reaction using an excess of diethylene glycol bis-chloroformate would have all chloride end groups on the molecules and could be analyzed for chloride content to determine the molecular weight. It was hoped that if an excess of diamine were used the condensation product would have all amine end groups and titration with hydrochloric acid could be used to determine the molecular weight. The titration of end groups to determine molecular weight follows the work of Carothers (6), who determined the

(6) W. H. Carothers, and F. J. Van Natta, J. Am. Chem. Soc. 55, 4714 (1933)

molecular weights of polyesters up to 26,700 by titrating the terminal carboxyl with alcoholic potassium hydroxide in chloroform solution. The only degree of uncertainty was the degree of homogeneity, which is high for crystalline solids and polymers with a long unit of the chain.

It was also hoped that the relationship of molecular weight to viscosity might be studied following the work of Staudinger and others (7,8).

This paper first presents the various preparations and fractionations of the condensation product of ethylene diamine with the diethylene glycol bis-chloroformate. Each preparation is followed by the properties investigated and the molecular weight runs made on that preparation. The results of the viscosity-molecular weight investigation follows. The condensation of hexamethylene diamine with diethylene glycol bis-chloroformate and some properties of this polymer are considered last.

(7) H. Mark, Determination of Viscosity (A. Weissberger, editor, Phys. Methods of Organic Chemistry Vol. I New York: Interscience Publishers, Inc. 1945) 14 pp.

(8) R. Fordyce and H. Hibbert, J. Am. Chem. Soc. 61, 1912(1939)

Preparation of Polymer I

A 500 cc. three-necked flask was provided with a mechanical stirrer, thermometer, and a 250 cc. dropping funnel. Fifteen and seven tenths grams (0.16 mole) of 60% ethylene diamine were put in the flask with 13.3 grams (0.33 mole) of sodium hydroxide in 100 cc. of tap water, Thirty eight and five tenths grams (0.17 mole) of diethylene glycol bis-chloroformate were added from the dropping funnel at about 15 drops per minute and with vigorous mechanical stirring. The reaction was exothermic and the temperature rose from 21° to 50° C. in the course of a half hour. At this point an ice-water bath was introduced to lower the reaction temperature. The temperature gradually fell to 16° C. at the end of the reaction time. The formation of small, white granules was observed as each drop of diethylene glycol bis-chloroformate hit the reaction surface and was suspended in the mixture.

The product was washed with water and allowed to dry in air. It lost weight continually over the course of a week and the odor of hydrogen chloride was clearly evident. This would indicate that the diethylene glycol bis-chloroformate, being insoluble in water, was occluded within the polymer granule and the amine end groups were in excess. On drying, thediethylene glycol bis-chloroformate was released and reacted with the amine end groups to liberate hydrogen chloride.

Preparation of Polymer I

Another possibility considered was the hydrolysis of the terminal chloroformate group by moisture from the air to liberate hydrogen chloride. This reaction was observed with a mixture of diethylene glycol bis-chloroformate and water. The water became acid to litmus and gave a positive chloride test. There was no appreciable change in the volume of chloroformate when the mixture was left standing overnight, indicating a slow rate of hydrolysis. Therefore 0.5 g. of Polymer I which had ceased to evolve hydrogen chloride and which gave a molecular weight of 5400 on chloride analysis, was mixed with 20 cc. of distilled water and distilled for 15 minutes with the distillate tube passing into a silver nitrate solution. Two more 20 cc. portions of water were added at 15 minute intervals so the total distillation time was 45 minutes. No precipitate formed in the silver nitrate solution and it was concluded that the polymer would not hydrolyze on drying in air.

The product was washed with ether to remove any excess chloroformate. On drying the odor of hydrogen chloride was still in evidence, confirming the theory of occlusion. After standing for two weeks the odor of hydrogen chloride was no longer evident. The yield was 26 g., 76% of the theoretical yield based on the reaction of one mole of ethylene diamine (60 g.) with one mole of diethylene glycol bis-chloroformate (231 g.) to liberate two moles of hydrogen chloride (73 g.) and give a resulting unit weight of 218 grams. The melting

Another possibility considered was the hydrolysis of the terminal chloroformate group by moisture from the air to liberate hydrogen chloride. This reaction was observed with a mixture of diethylene glycol bis-chloroformate and water. The water became acid to litmus and gave a positive chloride test. There was no appreciable change in the volume of chloroformate when the mixture was left standing overnight, indicating a slow rate of hydrolysis. Therefore 0.5 g. of Polymer I which had ceased to evolve hydrogen chloride and which gave a molecular weight of 5400 on chloride analysis, was mixed with 20 cc. of distilled water and distilled for 15 minutes with the distillate rose passing into a silver nitrate solution. Two more 20 cc. portions of water were added at 15 minute intervals so the total distillation time was 45 minutes. No precipitate formed in the silver nitrate solution and it was concluded that the polymer would not hydrolyze on drying in air.

The product was washed with ether to remove any excess chloroformate. On drying the odor of hydrogen chloride was still in evidence, confirming the theory of oxonium. After standing for two weeks the odor of hydrogen chloride was no longer evident. The yield was 52 g., 78% of the theoretical yield based on the reaction of one mole of ethylene diamine (60 g.) with one mole of diethylene glycol bis-chloroformate (231 g.) to liberate two moles of hydrogen chloride (73 g.) and give a resulting unit weight of 218 grams. The melting

range was 151-156° C. and on recrystallization from water was 152-159° C.

Properties of Polymer I

The polymer was found to be insoluble in ether, chloroform, ligroin, chlorobenzene, acetone, carbon tetrachloride, methyl alcohol, ethyl acetate, cyclohexanol, cyclohexanone, ethyl acetoacetate, nitroethane, d-limonene, tetrahydropyran, and butanol-1.

It was soluble in cold o-cresol, 90% formic acid, phenol, and a 1:1 mixture of o-cresol and butanol-1. It was slightly soluble in hot water, hot isopropyl urethane and hot N-nitroisopropyl urethane. It was soluble in the following hot solvents: methyl cellosolve, ethyl cellosolve, phenyl cellosolve, ethyl carbitol, N-nitroisopropyl amine, pyridine, formamide, nitrobenzene, 2-nitrobutanol, acetic anhydride, dichloro-ethyl ether,trioxane and anisole. It was hydrolyzed by hot dilute sodium hydroxide, hydrochloric acid, and nitric acid.

An attempt was made to identify the sodium hydroxide hydrolysis products which were believed to be sodium chloride, sodium carbonate, diethylene glycol and ethylene diamine. It was found that a mixture of 1.5 cc. of diethylene glycol with 1.5 cc. of 60% ethylene diamine in 10 cc. of 1% sodium hydroxide gave the benzenesulfonamide derivative of ethylene diamine when shaken with benzenesulfonyl chloride. If an excess of benzenesulfonyl chloride was used, it precipitated as a white solid in the alkaline medium and also in the

acidified filtrate. Both precipitates were recrystallized from a 33% ethyl alcohol solution and each had a melting point of 167-168° C. A mixture of the two products gave a mixed melting point of 167-168° C. The melting point of ethylene diamine benzenesulfonamide is 168° C. (9)

Therefore, 3 g. of polymer were hydrolyzed by refluxing with 3 g. of sodium hydroxide in 10 cc. of water for one hour. The clear solution was placed in a glass stoppered bottle and shaken with about 1 cc. of benzenesulfonyl chloride. A white solid precipitated. One cc. more of benzenesulfonyl chloride was added and the solid formed a liquid paste. The mixture was filtered and a crystalline precipitate formed in the filtrate upon acidification. This precipitate was washed with water and recrystallized from hot ethyl alcohol. The melting point was 167-168° C. A mixed melting point with the benzenesulfonamide of ethylene diamine previously prepared was found to be 167-168° C. and established ethylene diamine as one of the hydrolysis products.

An attempt was made to prepare the 3,5-dinitrobenzoate of pure diethylene glycol (10). A sample of technical diethylene glycol reacted with three sucessive portions of

(9) Shriner and Fuson, A Systematic Identification of Organic Compounds (second edition; New York: John Wiley and Sons Inc. 1940) p. 147.

(10) Milton Orchin, CA 37, 3020 (1943)

anhydrous calcium chloride with the liberation of considerable heat each time. Another sample was dried over two portions of potassium carbonate for two nights but did not become anhydrous. This sample was reacted with 3,5-dinitrobenzoyl chloride which could not be prepared without becoming unusually moist (11) due to the high humidity. The reaction failed due to the moisture present. Because so much difficulty was found in preparing anhydrous diethylene glycol from large quantities of technical diethylene glycol, it was decided to by-pass the identification of the 1.5 g. of diethylene glycol expected in the aqueous solution after the removal of the ethylene diamine from the 3.0 g. sample of polymer.

(11) same as (9) p. 138.

Purification of Polymer I

This condensation product was found to be slightly soluble in boiling water and recrystallized out on cooling. Because of the slight solubility (about 0.1 g. per 100 cc.) and the very slow filtering of the fine, powdery precipitate, purification of the polymer was not deemed practical by this method.

Although the polymer was readily soluble in hot methyl cellosolve, it was found that 0.3 g. dissolved in 120 cc. of solvent cooled to a solid gelatinous mass, unsuitable for recrystallization. Therefore the polymer was dissolved in hot methyl cellosolve and reprecipitated by slowly pouring the clear solution into a non-solvent such as water, acetone, ethyl alcohol or ether. A fine, white precipitate occurred in all cases. Filtering the water or ethyl alcohol from the mixture wasfound to be very slow. The acetone or ether was filtered more rapidly. As some of the ether was lost by evaporation on adding the hot methyl cellosolve, acetone was considered the best non-solvent for removing contaminants soluble in organic solvents and the water for removing inorganic contaminants. However, the inorganic salts were removed in this work by washing with water until the filtrate was neutral to litmus and/or did not give a chloride test with silver nitrate.

Molecular Weight of Polymer I

The molecular weight of Polymer I was determined by chloride analysis, assuming that an excess of the diethylene glycol bis-chloroformate had put a chloride group on each end of the molecule. Titration with standardized silver nitrate using dichlorofluorescein as the indicator was tried but the concentration of chloride ion was so small that the color change on the surface of the silver chloride was not sharp enough. This procedure might be satisfactory if a standard amount of chloride is added to give a sharp end point but because a pH adjustment was necessary after the alkaline hydrolysis of the polymer, the Volhard method was more satisfactory. Standard silver nitrate was tried in 0.0690 N solution and 0.00690 N solution. While the more dilute solution permitted more accuracy in measuring volume used it was found to give a very poor end point.

The polymer was believed free of diethylene glycol bis-chloroformate because the evolution of hydrogen chloride had ceased and when the polymer was mixed with boiling water and the mixture distilled into acidic silver nitrate solution there was no indication of a silver chloride precipitate. Whereas, when a single drop of chloroformate was put into 90 cc. of water and the water decanted from the drop and distilled into silver nitrate, a silver chloride precipitate was formed. Polymer I was washed with absolute alcohol and

alcoholic silver nitrate was added to a portion of the wash. A slight precipitate formed but this was attributed to the slight solubility of the polymer in alcohol, for when a portion of the wash was evaporated a trace of solid residue remained.

Standard silver nitrate solution was made by drying C. P. Baker silver nitrate for one hour at 110° C. and for two hours at 125° C. at the end of which time it had reached a constant weight of 11.7297 g. This weight was diluted to one liter at 20° C. for a .06903 N solution. This solution was titrated with approximately 0.05 N ammonium thiocyanate using 1 cc. of ferric alum indicator to the first brown tinge. One cc. of ammonium thiocyanate was found to be equivalent to 0.7190 cc. of silver nitrate from the following data:

Ammonium thiocyanate (cc.)

19.10-4.21 = 14.89 33.86-14.12 = 14.74 48.81-33.87 = 14.94

Silver nitrate (cc.)

15.26-4.53 = 10.73 26.08-15.41 = 10.57 36.82-26.08 = 10.74

One cc. of ammonium thiocyanate equals .7206 .7171 .7188 cc. of silver nitrate.

General procedure was to hydrolyze 0.6 g. of polymer with 0.6 g. of sodium hydroxide (analysis .001% chloride) in 30 cc. of distilled water under a reflux condenser for 30 to 45 minutes. The clear solution was acidified with 5 cc. of dilute nitric acid and a measured excess (5 cc. or more)

absolute alcohol was added to a portion of the wash.
A slight precipitate formed but only was attributed to the
slight solubility of the polymer in alcohol. For when a
portion of the wash was evaporated a trace of solid residue
remained.

Standard silver nitrate solution was made by drying
G. F. Baker silver nitrate for one hour at 110° C. and for
two hours at 150° C. at the end of which time it was treated
a constant weight of 11.7897 g. This weight was diluted to
one liter at 30° C. for a .06903 N solution. This solution
was diluted with approximately 0.05 N ammonium thiocyanate
using 1 cc. of ferric alum indicator to the first brown tinge.
One cc. of ammonium thiocyanate was found to be equivalent
to 0.7130 cc. of silver nitrate from the following data:

Ammonium thiocyanate (cc.)

Silver nitrate (cc.)

One cc. of ammonium thiocyanate equals
cc. of silver nitrate.

General procedure was to hydrolyze 0.8 g. of polymer
with 0.8 g. of sodium hydroxide (analysis .001% chloride)
in 20 cc. of distilled water under a reflux condenser for
30 to 45 minutes. The clear solution was acidified with 8 cc.
of dilute nitric acid and a measured excess (5 cc. or more)

of silver nitrate run in. Later the procedure was modified to 0.3 g. of polymer, 0.3 g. of sodium hydroxide, and 3 cc. of silver nitrate. The silver chloride was coagulated by heating on a steam bath and then filtered through quantitative filter paper (Whatman's 44) and washed with 3 portions of distilled water. The filtrate was titrated with ammonium thiocyanate using ferric alum as the indicator. Blank runs were made as follows:

Silver Nitrate (cc.)		
10.42	2.88	6.60
Ammonium thiocyanate (cc.)		
14.47 x .719 = 10.40	4.03 x .719 = 2.90	9.18 x .719 = 6.60

Most of the later runs were made with a 10 cc. buret graduated in 0.05 ml. and with a refraction pointed meniscus enabling accurate judgement of 0.01 ml. Maximum error between two readings should be 0.02 ml. therefore and these blank runs fall within experimental error. No correction was made for the blank.

Two runs were made on Polymer I following the general procedure:

Weight Polymer	31.0269 g. 30.3718 0.6551 g.	14.3470 g. 13.7256 0.6214 g.
$AgNO_3$ cc.	13.05 1.21 11.84	39.62 29.65 9.97
NH_4SCN cc.	13.10 1.50 11.60	25.82 16.50 9.32
Equiv. cc. $AgNO_3$	8.34	6.60
cc. $AgNO_3$ used	3.50	3.37
Molecular weight	5400	5350

The molecular weight was calculated as follows (from Run 1.):

3.50 cc. $AgNO_3$ x .0690 N = .2416 milliequivalents

.0002416 equivalents/ 2 chloride groups per molecule= .0001208 equiv. polymer

.6551 g. / .0001208 = 5400

This value is the weight number average molecular weight as it is based on the number of molecules in a weighed sample. It indicates that there are at least 24 units per molecule and an excess of .01 mole of diethylene glycol bis-chloroformate in an equivalent weight of 0.16 mole will insure all chloride endings. Also, the fact that some of the amine didn't react and was removed by the water washing and the occluded chloroformate reacted with the polymer on standing

Two runs were made on Polymer I following the general procedure:

Weight Polymer	0.8851 g.	0.8814 g.
	50.3713	17.7256
	51.2564	17.6070 g.
$AgNO_3$ cc.	11.64	9.87
	1.27	20.85
	12.91	29.72
NH_4SCN cc.	11.90	9.32
	1.30	10.90
	13.20	20.22
Equiv. cc. $AgNO_3$	6.36	6.80
cc. $AgNO_3$ used	6.80	9.87
Molecular weight	8400	8350

The molecular weight was calculated as follows (from Run I.):

6.80 cc. $AgNO_3$ x .0880 N = .5918 milliequivalents

.0008458 equivalents \ 2 chloride groups per molecule= .0004229 equiv. polymer

.8851 g. \ .0004229 = 8400

This value is the weight number average molecular weight as it is based on the number of molecules in a weighed sample. It indicates that there are at least 24 units per molecule and an excess of .01 mole of diethylene glycol bis-chloroformate in an equivalent weight of 0.18 mole VIII. Impure all chloride endings. Also, the face that some of the endo diene's react and was removed by the water washing and the resulted chloroformate reacted with the polymer on standing

would indicate all chloride endings. If some of the endings are amine, the molecular weight is too high. Chloride contamination would make the results too low.

Fractionation of Molecular Weights

Polymer I

Polymer I was fractionated by dissolving about 2 g. in 7 cc. of nearly boiling methyl cellosolve and pouring the clear solution very slowly into 50 cc. of acetone which was being swirled about in a flask. The precipitated fine, white powder was filtered off on a sintered glass funnel and was washed with acetone and ether. It was dried over phosphorus pentoxide for two days to a constant weight overnight. The solvents were examined for chloride content and gave no precipitate with alcoholic silver nitrate.

Three runs were made on this reprecipitated sample:

Wt. Polymer g.	21.6278 21.3593 0.2685	21.3593 21.1048 0.2545	15.9624 15.5928 0.3696
	3.50 0.70	6.50 3.52	6.06 0.13
$AgNO_3$ cc.	2.80	2.98	5.93
Equiv. cc. $AgNO_3$	1.86	2.10	4.70
cc. $AgNO_3$ Used	0.94	0.88	1.23
Molecular Weight	8300	8380	8630

This increase in molecular weight was due to either the removal of diethylene glycol bis-chloroformate contaminant, the solution of the lower molecular weight fraction in the methyl cellosolve-acetone mixture, the reaction of any amine end groups with chloride end groups at the higher temperature of the cellosolve solution, or the reaction between the

chloroformate groups and the cellosolve to release hydrogen chloride. The possible reaction between the chloroformate end groups of the polymer and the alcoholic group of the cellosolve was studied by mixing 0.5 g. of reprecipitated Polymer II (molecular weightabout 12,000 by chloride analysis) with 5 cc. of cellosolve. The mixture was heated to boiling and the distillate was passed into a silver nitrate solution for 3 or 4 minutes. No chloride precipitate was observed. This evidence indicates no reaction between the polymer and the cellosolve on heating. As approximately only half of the polymer was recovered from the reprecipitation it seemed likely this increase in molecular weight was due to loss of the lower molecular weight fraction in the solvent mixture.

Polymer I Fractionated Three Times

Five grams of Polymer I were dissolved in 50 cc. of hot methyl cellosolve and poured slowly into 200 cc. of ether to remove any chloroformate which might be present. The powdery precipitate was filtered and washed with two 5 cc. portions of ether. The precipitate dried to a gel in one hour, so it was triturated with ether to remove the methyl cellosolve. After washing with ether and drying in air for one week the melting range was 135-152° C., indicating some contaminant, probably the cellosolve. This product was redissolved in 120 cc. of methyl cellosolve and poured into 200 cc. of ether. The precipitate was filtered and washed well with ether. After

drying overnight its melting range was 148-159° C. The pure product was heated for one day at 110° C. to a constant weight. Only one molecular weight determination was made:

Weight polymer	20.8502	-	20.0965	= 0.7537 g.
cc. $AgNO_3$	7.00	-	0.50	= 6.50 cc.
cc. NH_4SCN	6.48	-	0.03	= 6.45 cc.
Equiv. $AgNO_3$	4.64 cc.			
$AgNO_3$ Used	1.86 cc.			
Molecular weight	11,800			

While this one run is not conclusive it is an indication of further fractionation with repeated solution and reprecipitation. This result was further confirmed by a later fractionation of the same polymer prepared under slightly different conditions, Polymer IV.

Preparation of Polymer II

It was decided to prepare a polyurethane similar to Polymer I but with amine rather than chloride end groups. Therefore 23.3 g. of 60% ethylene diamine (.23 mole) were dissolved in 125 cc. of tap water together with 13.3 g. (.33 mole) of sodium hydroxide. Then 38.5 g. of diethylene glycol bischloroformate (.17 mole) were added dropwise and with vigorous mechanical stirring. The reaction mixture was maintained at 12-22° C. by means of an ice-water bath. The addition was completed in 30 minutes and the product washed with cold water until neutral to litmus. It continued to lose weight and give

off hydrogen chloride, indicating that the chloroformate was again occluded and the excess diamine was removed by the water washing. The melting range was 144-158° C. and after recrystallization from water 154-160° C. The yield was 25.3 g. which is 70 % of the theoretical yield.

Five grams of Polymer II were melted in an oil bath at 160° C. for about one hour. Considerable hydrogen chloride was emitted at first but soon subsided. The white compound melted to a viscous liquid which continued to emit bubbles at a slow rate. The liquid could be drawn into a fine fiber by inserting a cold rod. The liquid solidified to a grayish-white mass on cooling and was broken up into granules. The compound was not powdery but rather tacky. After drying in a desiccator for one week its melting range was 138-148° C. After air drying for a month its melting range was 143-150° C.

Molecular Weight of Polymer II

After standing for three weeks, the odor of hydrogen chloride was not apparent and a hot water solution was not acid to litmus. A qualitative test indicated the presence of some chloride end groups and the following molecular weights were determined on the basis of all chloride end groups.

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
15.8596	4.99	5.98			
15.2860	0.14	0.15	3.47	1.38	12,200
.5736	4.85	4.83			

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol.Wt.
15.2860	9.89	5.03			
14.6814	4.99	0.13	3.52	1.38	12,800
0.6046	4.90	4.90			

These molecular weights are more than double those of Polymer I. This indicates that about half the end groups are chloroformate with the other half amine end groups. It was decided to heat this polymer with enough diethylene glycol bis-chloroformate to cause each amine end group to react with one molecule of the chloroformate. This would put chloride groups on the ends of all the molecules without increasing the molecular weight appreciably. Accordingly, 1 g. of diethylene glycol bis-chloroformate (mol. wt. 231) was added to 4.7 g. of the polymer (mol. wt. estimated about 5600 from Polymer I). The mixture was melted in an oil bath at 175° C. Considerable hydrogen chloride was in evidence. The mixture was cooled to 115° C. and one gram more of chloroformate added. The mixture was heated to 180° C. and allowed to cool. The product was triturated twice with ether, reprecipitated from hot methyl cellosolve into ether, and filtered through a sintered glass funnel. After drying at 115° C. to a constant weight the following molecular weights were obtained:

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
20.7749	5.43	3.65			
20.3750	0.75	0.14	2.52	2.16	5370
0.3999	4.68	3.51			

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
20.3750	5.97	8.11	3.15	2.69	5400
19.8735	0.13	3.73			
0.5015	5.84	4.38			

This molecular weight is probable the true molecular weight of Polymer II, reprecipitated once. Therefore the molecular weight of the crude Polymer II should be lower than crude Polymer I. We would expect a lower molecular weight on the basis of higher concentration of available diamine in the original solution from the general rule that the more of an excess of one reagent in a polycondensation, the lower the molecular weight of the product. (12)

(12) Paul O. Powers- Synthetic Resins and Rubbers (New York: John Wiley and Sons Inc. 1943) p. 27.

This molecular weight is probable the true molecular weight of Polymer II. Recrystallized once. Therefore, the molecular weight of the crude Polymer II should be lower than crude Polymer I. We would expect a lower molecular weight on the basis of higher concentration of available oxygen in the original solution from the general rule that the more of an excess of one reagent in a polycondensation, the lower the molecular weight of the product. (12)

(12) Paul J. Flory. Principles of Polymer Chemistry (New York: Cornell University Press, 1953) p. 67.

Preparation of Polymer III

Considerable occlusion of diethylene glycol bis-chloroformate occurred in the aqueous sodium hydroxide preparation of Polymers I and II. This occlusion and resulting delayed action placed chloride end groups on the polymer and also reduced the yield because of the unreacted diamine which was removed by washing with water. To minimize this occlusion, the diethylene glycol bis-chloroformate was diluted with acetone and the concentration of diamine was lowered by increasing the volume of water in the reaction mixture. An excess of 60% ethylene diamine, 14 g. (0.14 mole) was used to produce terminal amine groups. Ten grams of sodium hydroxide (.25 mole) were dissolved in 500 cc. of distilled water and the diamine added. The mixture was cooled to 10° C. in an ice-salt bath and 23.1 g. (0.10 mole) of diethylene glycol bis-chloroformate, dissolved in 200 cc. of acetone were added dropwise and with vigorous mechanical stirring. The addition was complete in three hours.

The fine, white, slightly gelatinous precipitate was filtered through sintered glass and was washed with acetone and triturated twice with ether. After drying over phosphorus pentoxide the yield was only 3.0 g. 14% of the theoretical. The filtrate of the preparation was examined for a further yield. The acetone was removed by water aspirator vacuum and a few tenths of a gram of polymer were precipitated. The

Preparation of Polymer III

Considerable cyclization of diethylene glycol bis-chloroformate occurred in the aqueous sodium hydroxide preparation of polymers I and II. This cyclization and resulting delayed action phased chloride end groups on the polymer and also caused the yield because of the unreacted diamine which was removed by washing with water. To minimize this cyclization, the diethylene glycol bis-chloroformate was diluted with acetone and the concentration of diamine was lowered by increasing the volume of water in the reaction mixture. An excess of 00% ethylene diamine, 1g. (0.14 mole) was used to produce tertiary amine groups. Ten grams of sodium hydroxide (.25 mole) were dissolved in 500 cc. of distilled water and the diamine added. The mixture was cooled to 10° C. in an ice-salt bath and 25.1 g. (0.10 mole) of diethylene glycol bis-chloroformate, dissolved in 200 cc. of acetone were added dropwise and with vigorous mechanical stirring. The addition was complete in three hours.

The fine, white, slightly gelatinous precipitate was filtered through sintered glass and was washed with acetone and triturated twice with ether. After drying over phosphorus pentoxide the yield was only 3.0 g. 14% of the theoretical. The filtrate of the preparation was examined for a further yield. The acetone was removed by water aspirator vacuum and a few beads of a gum of polymer were precipitated. The

basic solution was neutralized with acetic acid and evaporated on a steam bath to a small volume of liquid and solid. The solid was filtered off and washed with water. Most of the solid dissolved and was thought to be sodium hydroxide and sodium chloride. About half a gram of polymer was obtained in this way, to bring the yield to about 20%.

The polymer was hydrolyzed with sodium hydroxide, acidified with nitric acid and gave a heavy precipitate with silver nitrate. Therefore this method of preparation is no improvement over the other to attain all amine terminal groups. However, no odor of hydrogen chloride was noticed, indicating a more homogeneous reaction and little, if any, occlusion of chloroformate.

Preparation of Polymer IV

Polyurethanes were previously prepared from diols and diisocyanates (5) with monochlorobenzene as a solvent, the product separating after a reaction period of one hour. It was decided to repeat the preparation of Polymer I in a chlorobenzene solution with an excess of diamine to react with the hydrogen chloride liberated in place of the aqueous sodium hydroxide solution. The apparent solubility of the low molecular weight polyurethanes in chlorobenzene should result in a polymer of higher molecular weight than that of Polymer I. Diethylene glycol bis-chloroformate is soluble in chlorobenzene in all proportions but ehtylene diamine is not very soluble. Both are soluble in dioxane in all proportions and 1 cc. of ethylene diamine was found to be soluble in a mixture of 4 cc. of chlorobenzene with 11 cc. of dioxane. Therefore the diethylene glycol bis-chloroformate was diluted with chlorobenzene and the ethylene diamine was dissolved in dioxane in those proportions. This mutual solubility and dilution insures a more even reaction and should prevent the occlusion of the chloroformate previously noted. Twice the minimum equivalent of diamine was used.

Nine grams of ethylene diamine (10 cc.) (.09 mole) were dissolved in 110 cc. of 1,4-dioxane in a 500 cc. three-necked flask. Eleven and six tenths grams of diethylene glycol bis-chloroformate (.05 mole) were dissolved in 40 cc. of chlorobenzene and added at a rate of 50 drops per minute with

Preparation of Polymer IV

vigorous mechanical stirring. The reaction temperature was maintained at 28° C. by means of a water bath. Fine, white, sticky particles, seemingly swollen by solvent, were first seen on the sides of the flask above the reaction mixture. The addition was completed in 45 minutes and the stirring continued for 15 minutes more.

The solvent was filtered through a sintered glass funnel and the fine white powder washed with six 50 cc. portions of distilled water followed by three 15 cc. portions of acetone and three rinsings with ether. After air drying for two days, the polymer weighed 5 g., 50% of theoretical (.045 mole of unit weight 218). No odor of hydrogen chloride was apparent during this time and no indication of the occlusion of chloroformate encountered as in the previous preparations. The melting range of this product was 144-154° C. and reprecipitation from hot methyl cellosolve and acetone did not change it any. This range is slightly lower than that of Polymer I (151-150° C.) and Polymer II (154-160°C.).

Molecular Weight of Polymer IV

Polymer IV was placed in a desiccator over phosphorus pentoxide and attained a constant weight overnight after drying two days. The following molecular weight determination were then made:

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ cc. Used	Mol. Wt.
17.3076	9.96	2.10			
16.8216	6.50	0.50	1.15	2.31	6100
.4860	3.46	1.60			
16.8216	9.82	6.77			
15.4797	4.83	2.10	3.31	1.68	5900
.3419	4.99	4.67			

This molecular weight is, as expected, somewhat higher than that of Polymer I (5400) and Polymer II (5300). It was expected that a lower molecular weight fraction would be found in the original filtrate. On evaporation of the chlorobenzene-dioxane solvent under reduced pressure and temperature of about 50° C., one gram of fine, white powder was obtained. This powder was washed with three 10 cc. portions of acetone and three 15 cc. portions of water, the filtrate giving a negative chloride test with silver nitrate. The polymer was dried with ether and placed over phosphorus pentoxide for six days. The following molecular weights were then obtained:

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
26.2066	2.42	3.16			
25.9970	0.02	0.00	2.27	0.13	49,000
0.2096	2.40	3.16			
25.9970	4.97	6.43			
25.7570	2.51	3.18	2.34	0.12	58,000
.2400	2.46	3.25			

These surprisingly high molecular weights could only be explained by the possibility that many of the end groups were not chloride, but amine groups. To test for an excess of diamine the water washings of the original preparation were diluted to 300 cc., and 10 cc. portions titrated against 0.0988 N hydrochloric acid. Two titrations were made using methyl red as the indicator.

cc. HCl		N HCl
3.95	8.24	0.0988
0.05	4.28	
3.90	3.96	

3.93 cc. x .0988 x 30 x .030 = 0.35 g. diamine

An excess of 0.35 g. diamine in the water washings indicated a certain excess of diamine in the original filtrate. Probably the diamine reacted with most of the chloride end groups on standing for four days or on heating to 50° C. for the evaporation of the solvent. This would leave few chloride end groups and result in the apparent high molecular weight in the filtrate polymer.

Molecular Weight of Polymer IV

Fractionated Once

Two grams of Polymer IV were mixed in 10 cc. of hot water and filtered to remove any soluble chloride and to dissolve any low molecular weight polymer. The powder was filtered and washed with water, acetone and ether. After drying it was dissolved in 10 cc. of hot methyl cellosolve and the clear solution slowly poured into 50 cc. of agitated acetone. The mixture was cooled in ice-water and the fine precipitate filtered and washed with ether. It was dried over phosphorus pentoxide for one week to a weight of 1.7 g. A water wash of the polymer gave a negative chloride test with silver nitrate. The following molecular weights were obtained:

Weight	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
16.2749	7.47	8.45			
15.9849	4.98	6.55	1.37	1.12	7500
.2900	2.49	1.90			
15.6915	3.00	9.12			
15.3975	0.01	6.60	1.81	1.18	7200
.2940	2.99	2.52			

These molecular weights are higher than those of the original product due to the solubility of the lower molecular weight polymers in the hot water and the methyl cellosolve-acetone mixture.

Molecular Weight of Polymer IV
Fractionated Three Times

Accordingly, some of the original polymer was reprecipitated three times to check on the high molecular weight of Polymer I on which only one run was made. One gram of polymer was dissolved in 10 cc. of hot methyl cellosolve and slowly poured into 50 cc. of distilled water. The mixture was cooled in an ice-bath and the precipitated polymer filtered and washed with acetone and ether. It was redissolved in 10 cc. of hot methyl cellosolve and reprecipitated in 50 cc. of acetone. The precipitate was filtered and dissolved a third time in hot methyl cellosolve. Not all of the polymer went into solution this time and the mixture was filtered hot into 25 cc. of distilled water. The precipitate was washed with water, the filtrate giving a negative chloride test with silver nitrate. It was dried with ether and placed over phosphorus pentoxide. After two days it attained a constant overnight weight of 0.7 g. The molecular weights were:

Weight	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol. Wt.
25.7141	2.50	7.45			
25.5703	0.12	4.72	1.96	0.42	9,900
.1438	2.38	2.73			
25.5703	5.02	3.12			
25.4618	2.50	0.01	2.24	0.28	10,000
.1085	2.52	3.11			

This further increase in molecular weight substantiates the theory of solubility of low molecular weight fractions in

the process of reprecipitation for high molecular weights.

Preparation Of Polymer V

To determine the effect of temperature on molecular weight of polyurethanes prepared from ethylene diamine and diethylene glycol bis-chloroformate, Polymer V was prepared. Following the procedure used for Polymer IV, an excess of diamine was used in place of the sodium hydroxide and water used for Polymers I, II, and III. This procedure eliminated the possibility of hydrolysis due to sodium hydroxide at high temperatures. The same quantities were used: 9 g. of ethylene diamine (0.09 mole) dissolved in 110 cc. of 1,4-dioxane, and 11.6 g. of diethylene glycol bis-chloroformate (0.05 mole) dissolved in 40 cc. of chlorobenzene. The reaction temperature was maintained at 82° C. by means of a steam bath.

A mass of white granules was first seen on the tip ofthe dropping funnel due to the reaction with the diamine vapor as the chloroformate entered the flask. After adding about 1/3 of the chloroformate, fine, white granules began splashing onto the sides of the flask. The color of these granules gradually changed from white to a creamy yellow. The addition was complete in 45 minutes and the stirring continued for 15 minutes more. The mixture was cooled in an ice-water bath and filtered through sintered glass. It was washed with 80 cc. of acetone in several portions and with 200 cc. of water in several portions. The yield was only 2.5 g., 25% of the theoretical yield, indicating that much of the polymer stayed

in solution. The melting range of this polymer was 150-155° C.

Fractionation of Molecular Weights

Polymer V

The water washings of the polyurethanes was very slow as the very fine, sticky powder settled and blocked the sintered glass filter. To facilitate the washings, the supernatant water in the filter, together with some of the top layer of polymer, was decanted. This was repeated until a filtrate of the polymer remaining in the filter funnel gave a negative chloride test. This polymer was dried with ether and placed over phosphorous pentoxide overnight. The molecular weight was as follows:

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc. $AgNO_3$	$AgNO_3$ Used cc.	Mol.Wt.
25.4680	6.01	5.87			
25.1521	3.00	3.10	1.99	1.02	8980
.3159	3.01	2.77			
25.1521	9.04	8.95			
24.8928	6.01	5.92	2.18	0.85	8940
.2593	3.03	3.03			

This molecular weight is significantly higher than that of Polymer IV (6000) which was prepared at 28° C. This higher molecular weight could have been caused by the decantation of a lower molecular weight fraction along with the water washing. Therefore the decanted water and polymer were separated by centrifuging and decanting until the water decanted gave a negative chloride test after being clarified by fil-

tration. The polymer fraction was then dried with absolute slcohol and ether and placed over phosphorous pentoxide for two days. The following molecular weight runs were then made:

Wt. Polymer	$AgNO_3$ cc.	NH_4SCN cc.	Equiv. cc.$AgNO_3$	$AgNO_3$ Used cc.	Mol.Wt.
24.9616	7.53	2.43			
24.7678	5.05	0.05	1.71	0.77	6950
.1938	2.48	2.38			
24.7678	9.92	4.62			
24.5674	7.53	2.47	1.55	0.84	6910
.2004	2.39	2.15			

This molecular weight confirms the possibility of fractionating the polymer by sedimentation. The procedure is just as rapid as the reprecipitation method and provides an additional advantage in the easy recovery of the lower molecular weight fraction. This lower molecular weight fraction has a higher molecular weight than the crude Polymer IV (6000) and confirms the higher molecular weight obtained by carrying out the condensation in organic solvents at an elevated temperature.

Viscosity-Molecular Weight Investigation

Staudinger (7) related the relative increase of the viscosity (n_o) of a pure solvent to the viscosity (n_c) of a solution with concentration (c) in grams/100 ml. of solution by the equation:

$$n_{sp} = (n_c) - (n_o) / n_o$$

where (n_{sp}) is called the specific viscosity. In terms of time of efflux (t) of the two liquids involved at a constant pressure the equation becomes:

$$n_{sp} = (t_c - t_o)/ t_o$$

Staudinger's rule postulates that the molecular weight of a high polymer is directly proportional to its viscosity in dilute solution:

$$\frac{n_{sp}}{c} = KM$$

where K is a constant. Recent investigators (8) have shown that this relationship holds for concentrations of less than 5 g. polymer per 100 ml. of solution for polymers up to 8000 in molecular weight.

It was therefore decided to check the relationship of the various molecular weights established by the chloride titrations and to establish the value of K by means of viscosity measurements. o-Cresol was chosen as the pure solvent. Four hundred cc. of practical o-cresol were distilled through a 4 foot refluxing column packed with broken glass and wound with resistance wire which enabled heating to within a few degrees of the distillation temperature. The column was

insulated by two dead air spaces and the distillate collected under a reflux ratio of about 3 to 1 at the top of the column. The middle fraction of 180 cc. was collected at 189.8-190.2°C. The literature gives the boiling point of o-cresol as 191-192° C. The index of refraction n_{20}^{D} 1.5450 compared with n_{20}^{D} 1.5453 given in the literature.

Six cc. of the solvent or solution was used in the Ostwald viscometer and allowed to come to the temperature of the thermostat (33.3°C. ± 0.1°C) for about one hour. Solutions were made by dissolving about 0.1 g. of polymer in 10 cc. of pure o-cresol. The fastest time of efflux was taken as the most probable value in cases where it drifted. The solutions were filtered to remove any foreign matter.

Solution	Mol. Wt.	Wt. Polymer	Time of Efflux			n_{sp}/c
o-Cresol	-----	-----	8:06.9 8:06.5	8:07.8 8:06.9	8:07.1 8:06.5	---
Polymer I	5400	.1026	9:37.4	9:37.6	9:37.6	1.81
Polymer IV	6000	.1446	10:38.7	10:38.8	10:38.6	2.15
Polymer V	6900	.1068	9:48.6	9:48.6	9:48.6	1.97
Polymer IV	7300	.0833	9:42.0	9:43.6	------	2.36
Polymer I	8300	.0840	9:25.8	9:27.3	9:27.8	1.94
Polymer V	9000	.1191	10:41.8	10:40.0	10:41.8	2.65

An example calculation for Polymer I (5400):

Time for solvent efflux (t_o) 8:06.6

Time for solution efflux (t_c) 9:37.5

$n_{sp} = (t_c - t_o)/t_o = 91.0/487 = .187$ $\quad n_{sp}/c = .187/.1026 = 1.81$

$c = .1026$ g./10 cc.

These relative viscosities prove the molecular weights obtained by chloride titration invalid. This indicates that the fundamental assumption of all chloride end groups on the polymers prepared is wrong. There are therefore some terminal amine groups present and the proportion of these groups to chloride groups varies with the method of preparation. Therefore, to make an analysis of these molecular weights valid, an amine as well as a chloride analysis must be made on each polymer. If equivalent weights of the same polymer are used for analysis, the molecular weight can be obtained from:

$$M = \frac{\text{Wt. polymer}}{\text{Equiv. } AgNO_3 + \text{Equiv. HCl}}$$

A qualitative test indicated that the polymer may be dissolved in o-cresol and titrated with alcoholic hydrochloric acid using thymol blue (pH 2) as the indicator.

The viscosities of the original Polymers I, IV and V roughly follow their molecular weights as determined by chloride titration. Therefroe the conclusions as to merits of preparation based on these molecular weights still hold good though the actual value of molecular weight is invalid.

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$$M = \frac{\text{Wt. polymer}}{\text{equiv. } AgNO_3 \text{ equiv. wt.}}$$

A qualitative test indicated that the polymer may be dissolved in o-cresol and titrated with alcoholic hydrochloric acid using thymol blue (pH 2) as the indicator.

The viscosities of the original Polymers I, IV and V roughly follow their molecular weights as determined by chloride titration. Therefore the conclusions as to merits of preparation based on these molecular weights still hold good though the actual value of molecular weight is invalid.

Preparation of Polymer VI

Eight grams of sodium hydroxide (.20 mole) and 11.6 g. of hexamethylene (.10 mole) diamine were dissolved in 300 cc. of tap water and cooled in an ice-water bath to 12° C. Twenty eight and seven tenths grams of diethylene glycol bis-chloroformate (.125 mole) were added dropwise and with good mechanical stirring. The addition took 45 minutes. The product was a large, fibrous-like ball and some smaller granules. It was triturated to a smooth paste with water and washed until neutral to litmus. The odor of the chloroformate was quite evident and the polymer was triturated with two portions of ether. As with Polymers I and II, the odor of hydrogen chloride was very strong as this product dried. The melting range was 118-124° C., compared to 120° C. reported from the preparation of this polymer from hexamethylene diisocyanate and diethylene glycol (2).

The yield was 13.8 g., only 50% of the theoretical. In general higher yields seemed to have been obtained at higher reaction temperatures, provided of course the temperature does not go high enough to cause hydrolysis with the sodium hydroxide.

This polymer, unlike the others prepared, could not be hydrolyzed with sodium hydroxide, even at a 30% concentration for 30 minutes. It is hydrolyzed by cold concentrated sulfuric acid and by hot dilute sulfuric acid.

Preparation of Polymer VI

Eight grams of sodium hydroxide (.20 mole) and 11.6 g. of hexamethylene (.10 mole) diamine were dissolved in 300 cc. of tap water and cooled in an ice-water bath to 12° C. Twenty eight and seven tenths grams of diethylene glycol bischloroformate (.158 mole) were added dropwise and with good mechanical stirring. The addition took 45 minutes. The product was a large, fibrous-like ball and some smaller granules. It was triturated to a smooth paste with water and washed until neutral to litmus. The odor of the chloroformate was quite evident and the polymer was triturated with two portions of ether. As with Polymers I and II, the odor of hydrogen chloride was very strong as this product dried. The melting range was 113-114° C., compared to 130° C. reported from the preparation of this polymer from hexamethylene diisocyanate and diethylene glycol (2).

The yield was 17.6 g., only 90% of the theoretical. In several higher yields seemed to have been obtained at higher reaction temperatures, provided of course the temperature does not go high enough to cause hydrolysis with the sodium hydroxide.

This polymer, unlike the others prepared, could not be hydrolyzed with sodium hydroxide, even at a 30% concentration for 30 minutes. It is hydrolyzed by cold concentrated sulfuric acid and by hot nitric sulfuric acid.

Polymer VII

This polymer was prepared as Polymer VI but with an excess of hexamethylene diamine rather than diethylene glycol bis-chloroformate. A solution of 3.2 g. of sodium hydroxide (.08 mole) was mixed with 5.8 g. of hexamethylene diamine (.050 mole) and the mixture cooled to 0° C. with an ice-salt bath. Then 10.4 g. of diethylene glycol bis-chloroformate (.045 mole) were added dropwise and with good mechanical stirring. The addition took 30 minutes and the temperature had risen to only 3°C. Most of the yield coagulated in one large lump which floated on the surface and a large mass which formed on the stirring rod. The product was filtered and triturated with water and ether. It gave off a strong odor of hydrogen chloride on drying and weighed 6.7 g. which is 55% of the theoretical yield.

The filtrate from the reaction was further reacted with 8.0 g. of diethylene glycol bis-chloroformate (.03 mole) to form an additional 4.3 g. yield from the unreacted hexamethylene diamine. This yield added to the original brings the total yield up to 81% based on the hexamethylene diamine as the minimum chemical.

Four grams of this polymer were melted at 160° C. for one hour. A considerable evolution of hydrogen chloride took place at first but after about 15 minutes the viscous liquid smelled rather pleasant. By inserting a cold rod the liquid

could be drawn into a fine fiber. This polymer lost about 0.5 g. due to the liberation of hydrogen chloride. Catlin (2) reported this polymer from the preparation of diol and di - isocyanate to have an intrinsic viscosity of .31 and a cold drawn fiber to have a tensil strength of .02 g./dernier on break dimensions.

Findings and Conclusions

A polycondensation of ethylene diamine or of hexamethylene diamine with diethylene glycol bis-chloroformate has been accomplished. An aqueous solution of an equivalent weight of sodium hydroxide or equivalent excess of diamine was used to combine with the hydrogen chloride liberated in the reaction. The use of excess diamine and an organic solvent for both the diamine and the chloroformate caused a smoother reaction and prevented the occlusion of chloroformate so evident in the aqueous preparation. The yields of the aqueous sodium hydroxide preparation with ethylene diamine were higher (70-76%) than those of the preparation with organic solvents (14-50%), due to the solubility of the lower molecular weight fraction in these solvents. The yields with hexamethylene diamine and aqueous sodium hydroxide were (50-55%).

The polyurethanes prepared by this reaction were in general insoluble in organic solvents, excepting such acidic compounds as phenol, cresol and formic acid. The polymer of ethylene diamine and diethylene glycol bis-chloroformate was easily hydrolyzed by acids and bases while that of hexamethylene diamine and the chloroformate was hydrolyzed by acid but not by base.

Two methods of fractionating the polyurethanes were found. The polyurethanes could be dissolved in hot cellosolve and reprecipitated by pouring slowly into a non-solvent.

This resulted in the solution of the lower molecular weight fraction. A better method was found to be the fractionation by rate of sedimentation. The higher molecular weight fraction settles first in an aqueous suspension in a sintered glass funnel.

The molecular weights of the polyurethanes could not be obtained by using an excess of chloroformate and analyzing for chloride terminal groups because some of the molecules were terminated with the amine group. This was proven by a comparison of the molecular weights obtained by chloride analysis with the relative viscosities of the mdecular weight fractions dissolved in o-cresol. However the molecular weights based on chloride titrations allow comparison of the molecular fractions of any one polymer preparation.

It is believed that an accurate molecular weight may be found by titrating equal weights of polymer for chloride content and for amine content. The polymer could be dissolved in cresol and titrated with alcoholic hydrogen chloride using thymol blue (pH 2) as the indicator.

The relative viscosities of the molecular weight fractions showed that Polymer I, prepared in aqueous sodium hydroxide, has a lower molecular weight than Polymer IV, prepared in organic solvents with an equivalent excess of diamine at room temperature, and that Polymer V, prepared exactly like Polymer IV but at 82° C., has the highest molecular weight since the larger fraction of that preparation had the

highest viscosity.

SUMMARY

A polycondensation of hexamethylene diamine and diethylene glycol bis-chloroformate has been carried out in the presence of aqueous sodium hydroxide with yields of 50 and 55% on the basis of chloroformate and diamine respectively. The melting range and fiber forming properties of this polymer agree with those reported (2) by the condensation of hexamethylene diisocyanate with diethylene glycol under nitrogen at 250° C. It is hydrolyzed by acid but not by base.

A polycondensation of ethylene diamine and diethylene glycol bis-chloroformate was also carried out. This polymer has not been previously reported. Its melting range is 150-160° C. It is not soluble in most organic solvents but is easily hydrolyzed by both acid and base. This reaction was carried out in two ways:

(1) The diethylene glycol bis-chloroformate was added dropwise to an aqueous solution of an equivalent weight of diamine and sodium hydroxide. The addition was accomplished with good mechanical stirring. The reaction was exothermic and the temperature was maintained around 10° C. by means of an ice bath. These yields were 70 and 76%. Much of the chloroformate was occluded in the polymer granules as indicated by the liberation of hydrogen chloride on drying.

(2) The diethylene glycol bis-chloroformate was

dissolved in chlorobenzene and added dropwise and with good mechanical stirring to a solution of twice the equivalent weight of ethylene diamine in dioxane solvent. The reaction was carried out at 82° C. and at room temperature and the yields were 25 and 50% respectively due to the solubility of the polymer in the solution. In these reactions there was no indication of occlusion.

The polyurethanes were purified by washing and/or triturating with water to remove all water-soluble salts. The polymers were then allowed to stand until all of the occluded chloroformate had reacted or evaporated. Any chloroformate still present was removed in the first fractionation with methyl cellosolve.

The polymers were fractionated by:

(1) Solution in hot solvent and reprecipitation of the higher molecular fraction in a non-solvent.

(2) Rate of sedimentation.

Molecular weight determinations based on the analysis of chloride content on polymers prepared with an excess of chloroformate were only relative. Viscosity relationships werecarried out by comparing the time of efflux of o-cresol with that of weighed amounts of polymer in o-cresol (concentrations of about 1% were employed). These relationships indicate that amine analysis must also be made to obtain the correct molecular weights of the polyurethanes.

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